

REAL TIME CHARGE EFFICIENCY MONITORING FOR NICKEL ELECTRODES IN NICKEL AND NICKEL-HYDROGEN CELLS

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Introduction

The charge efficiency of nickel-cadmium and nickel-hydrogen battery cells is critical in spacecraft applications for determining the amount of time required for a battery to reach a full state of charge. The charge efficiency is the amount of charge stored relative to the amount being input to the battery by the battery charging system. As nickel-cadmium or nickel-hydrogen batteries approach about 90% state of charge or higher, the charge efficiency begins to drop towards zero, making estimation of the total amount of stored charge uncertain. Knowledge of the charge efficiency during real time operation could provide switch points for switching to trickle charge with minimum overcharge, battery charge control data for autonomous operation, or could allow automatic battery problem detection and responses in intelligent systems.

For nickel-cadmium batteries, which constitute most of the existing data base for space flight battery experience, it is difficult to accurately determine charge efficiency on a real time basis during uninterrupted operation. Charge efficiency estimates are typically based on prior history of available capacity following standardized conditions for charge and discharge. These methods work well as long as performance does not change significantly. Such performance changes may however make battery operation difficult as the batteries degrade towards the end of their life. The situation is potentially better for nickel-hydrogen batteries, for which internal cell pressures can provide an indication of the amount of charge stored. However such pressures can drift over long periods of operation, pressure monitoring hardware on each cell can be quite heavy, and the reliability of pressure monitoring strain gauges has been a problem. Thus a relatively simple method for determining charge efficiencies during real time operation for these battery cells would be a tremendous advantage. Furthermore such a method should ideally require monitoring of nothing more than the voltages of the battery cells. Such a method has been explored in this work, and appears to be quite well suited for application to nickel-cadmium and nickel-hydrogen battery cells.

Method for Determining Charge Efficiency

The charge efficiency of a nickel-cadmium or nickel-hydrogen cell that is nickel electrode limited as full charge is approached is given by

$$N = 1 - I_{ox}/I \quad (1)$$

where N is the fraction of the current I that is being stored in the cell. I_{ox} is the current going into evolution of oxygen, i. e. overcharge. The oxygen evolution current may be determined from the cell voltage using a

standard Tafel expression, assuming that the potential of the negative electrode does not change significantly as the cell goes into overcharge.

$$I_{ox} = I_0 \exp(KV) \quad (2)$$

where I_0 and K are empirically determined constants that define the rate of oxygen evolution as a function of cell voltage. These constants may be conveniently measured or updated without discharging the battery cell simply by measuring the cell voltage as a function of current when the cell is fully charged, a condition that causes all the current to go into oxygen evolution.

Cell Tests

The method outlined above was tested using both laboratory cells and sealed 6Ah NiCd cells. The laboratory cells had a nickel electrode, a Hg/HgO reference electrode, and a nickel metal counter electrode, and used 31% KOH as electrolyte. The temperature of all cells tested was controlled to within ± 0.1 deg C using a regulated temperature bath that pumped cooling fluid through a copper block into which the cells were mounted. All tests were both controlled and monitored by a microprocessor, which operated from an uninterruptible power system. Independent under- and over-voltage interlocks were included in the system for cell safety in the event of an equipment malfunction.

The first tests that were done involved simply charging the cell followed by discharge at a C/2 rate (the C rate discharges the nameplate cell capacity in a one hour period). Typical voltages during charge at a C/10 rate for both laboratory cells and a 6 Ah NiCd cell are indicated in Fig. 1. While the cell was at a full state of charge, the current/voltage curve for oxygen evolution was measured by reducing the current from the C/10 charge rate to C/20, C/50, and C/100. At each charge rate the cell voltage was allowed to stabilize before being recorded. The steady-state oxygen evolution voltages were corrected for the ohmic voltage drops within the cell, which was a negligible correction for charge rates of C/10 or lower. The capacity stored in the cell was plotted as a function of time on charge at a C/10 rate. Typical data are indicated in Figs. 2 and 3 for 0 deg C and 23 deg C operation of the laboratory cells. Using the measured voltages during recharge with the measured oxygen evolution current/voltage curves, the charge efficiency was calculated from Eq. (1) and the total stored capacity was compared to the data of Figs. 2 and 3. This procedure gave good agreement with the experimental results as long as the voltage rollover observed as the cell went into overcharge was not significant, such as at 0 deg C. Voltage rollover is defined in Fig. 1. The voltage rollover observed in both laboratory cells and sealed NiCd cells was taken into account by assuming that this effect was due to an offset in the overcharge voltage that occurred as the state of charge increased to where oxygen began to be given off. Such an offset could arise from changes in the nickel electrode as it goes into oxygen evolution, or from changes in the negative electrode potential resulting from the oxygen generation. When such a voltage offset correction was applied by subtracting the offset from the voltages measured prior to rollover, excellent agreement was obtained between the measured capacity and that calculated. (At rollover the offset was exponentially attenuated according to the width of the rollover peak). The calculated results are indicated in Figs. 2 and 3 for both capacity and charge efficiency as a function of charge time. Calculations were also done that optimized the agreement between the data and the calculated results

by adjusting the amplitude of the voltage offset. These calculations indicated that optimum agreement was obtained when the offset was the same as the amplitude of the voltage rollover.

The results of similar tests for a 6 Ah NiCd cell are indicated in Fig. 4 at 23 deg C. While the amplitude of the voltage rollover is greater in this cell than in the laboratory cells of Figs. 2 and 3, excellent agreement between the measured and the calculated capacity is obtained when the overcharge potentials are corrected for the amplitude of the voltage rollover. The data of Figures 1-4 indicate that while the voltage behavior during charge may be significantly affected by both temperature and prior cell history, the measured voltage behavior maintains a good correlation with the charge efficiency characteristics.

The capability to predict charge efficiencies from voltage for a single cycle is of some use, however of more practical use is the ability to determine charge efficiencies during continuous cycling, which is how battery cells are used in space applications. The most sensitive test of the charge efficiency calculation is to charge a cell to near full charge, then to cycle it a number of times at about 50% DOD using a charge return of 100.0%. Since no additional charge is being returned to compensate for overcharge (oxygen evolution), the cell should gradually decrease in state of charge. This test was done for both laboratory cells and a 6 Ah NiCd cell. After 12 cycles the cell was discharged to determine its state of charge. The voltage of the cell during the cycling was used to calculate the state of charge and charge efficiency continuously during the cycling, giving the results in Figs. 5 and 6 for the laboratory and 6 Ah cells respectively. The agreement between the measured capacity after the cycling and that calculated from the cell voltage alone is excellent. The current voltage relationship used to determine oxygen evolution as a function of voltage was determined both before and after the 12 cycles, and was found to only exhibit small changes with cycling. Such changes in oxygen evolution voltages are likely to occur quite slowly during long-term cycling, and may be easily considered in charge efficiency calculations by periodically measuring the overcharge voltage as a function of current.

Requirements for System Application

For the method evaluated here to be applied to determining charge efficiency and state of charge in a battery system, several requirements must be met. The first of these is that individual cell voltages be provided to a processing facility, whether on the ground or part of the power system. The system must also have the ability to periodically determine the overcharge voltage as a function of current. This can be done when the battery is at full charge during sunlit periods for geosynchronous applications. For low-earth orbit applications such measurements may be possible during trickle charge or by varying the VT level while the battery is fully charged. In systems where temperatures may vary significantly during recharge, methods to correct the magnitude of the voltage rollover as a function of temperature must be established. The evaluation of such methods in life tests can provide data to indicate how well they work over long term operation.

Conclusions

A method has been demonstrated to effectively allow the charge efficiency of

NiCd and NiH₂ cells to be monitored in real time, using only voltage measurements as inputs. With further evaluation such a method may provide a means to better manage charge control of batteries, particularly in systems where a high degree of autonomy or system intelligence is required.

Charge Voltages for Laboratory and 6 Ah NiCd Cells

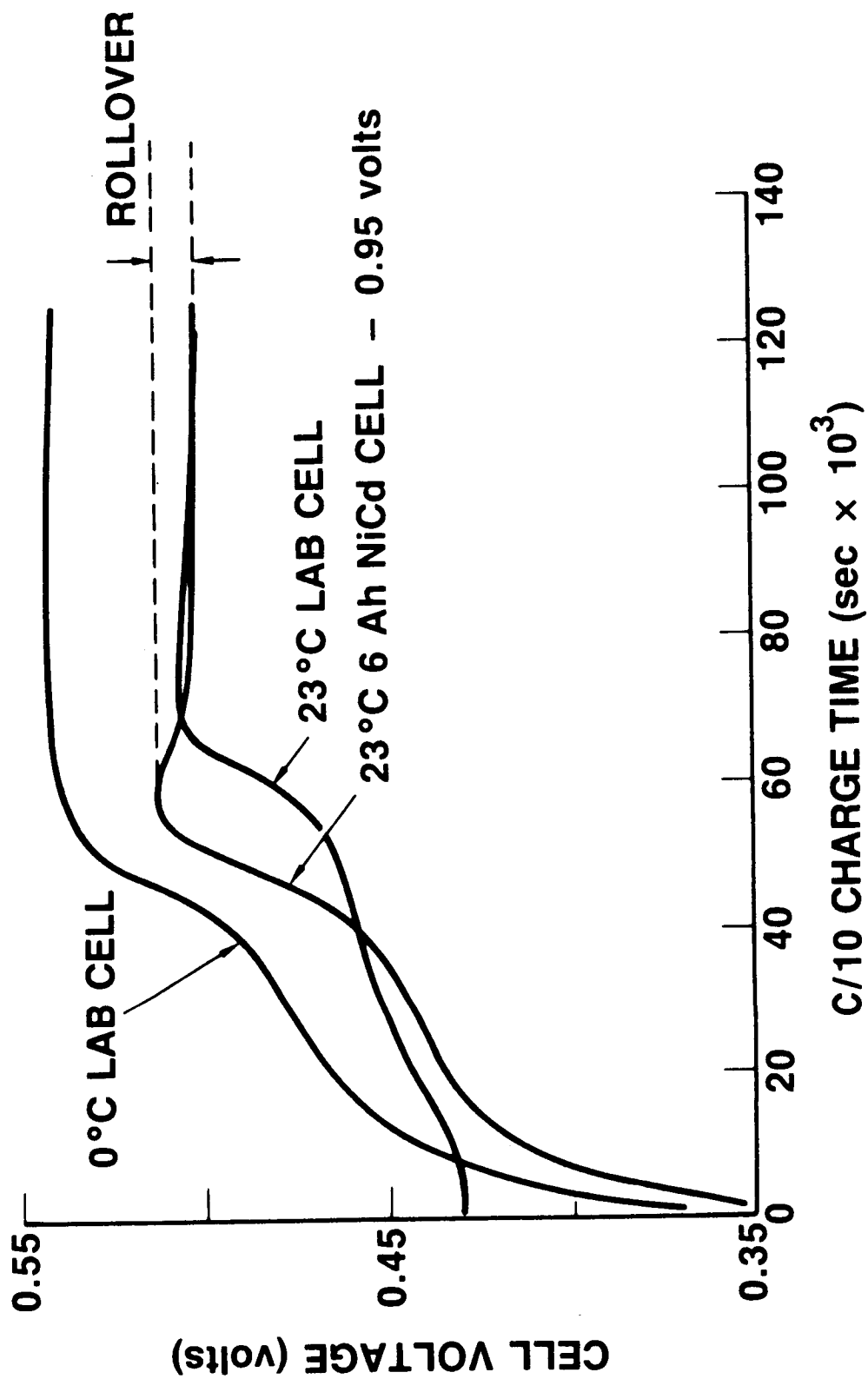


Figure 1.

Capacity and Charge Efficiency as a Function of Charge Time at C/10 (2mA/cm²) for Nickel Electrode

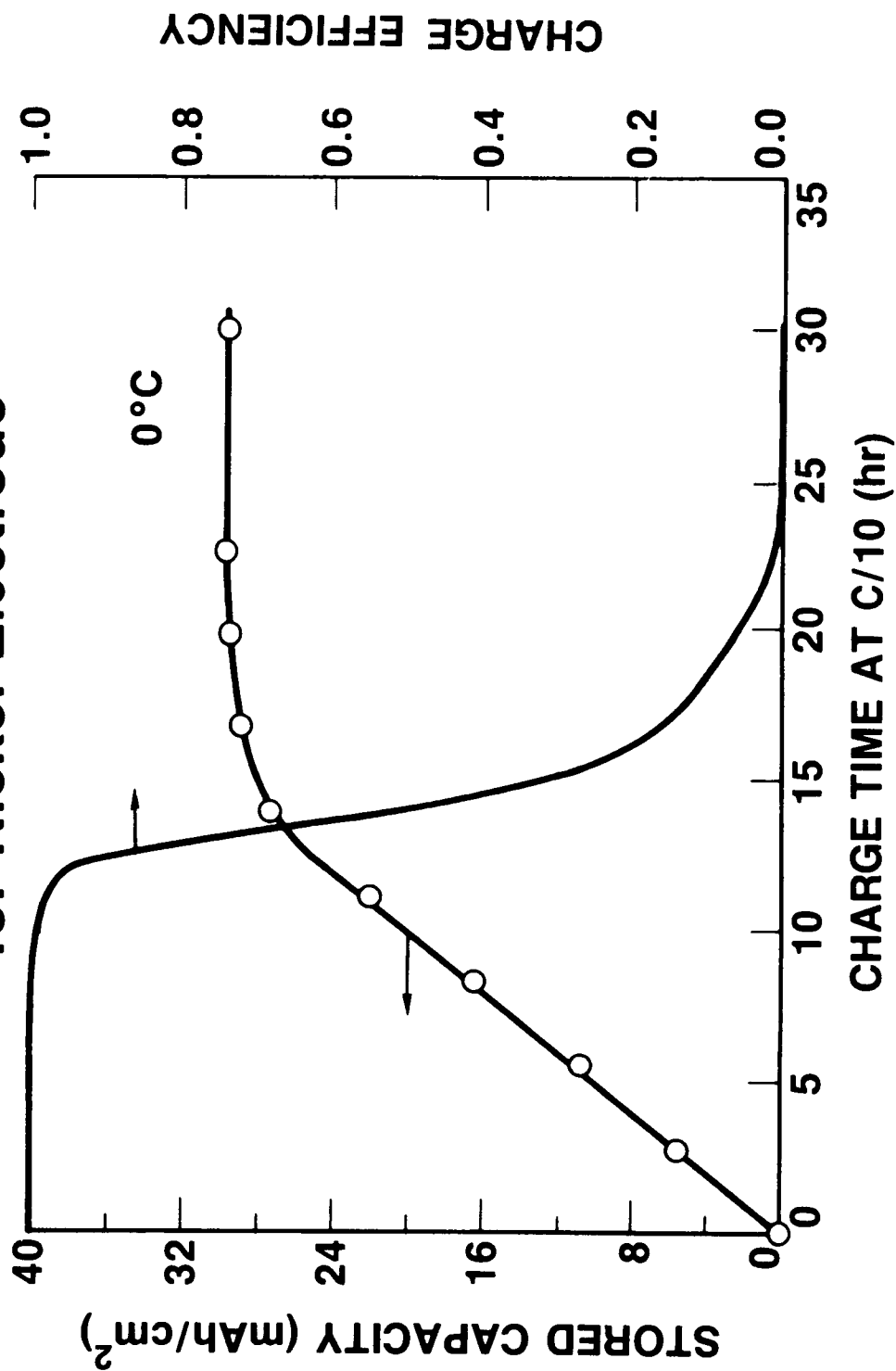


Figure 2.

Capacity and Charge Efficiency as a Function of Charge Time at C/10 (2mA/cm²) for Nickel Electrode

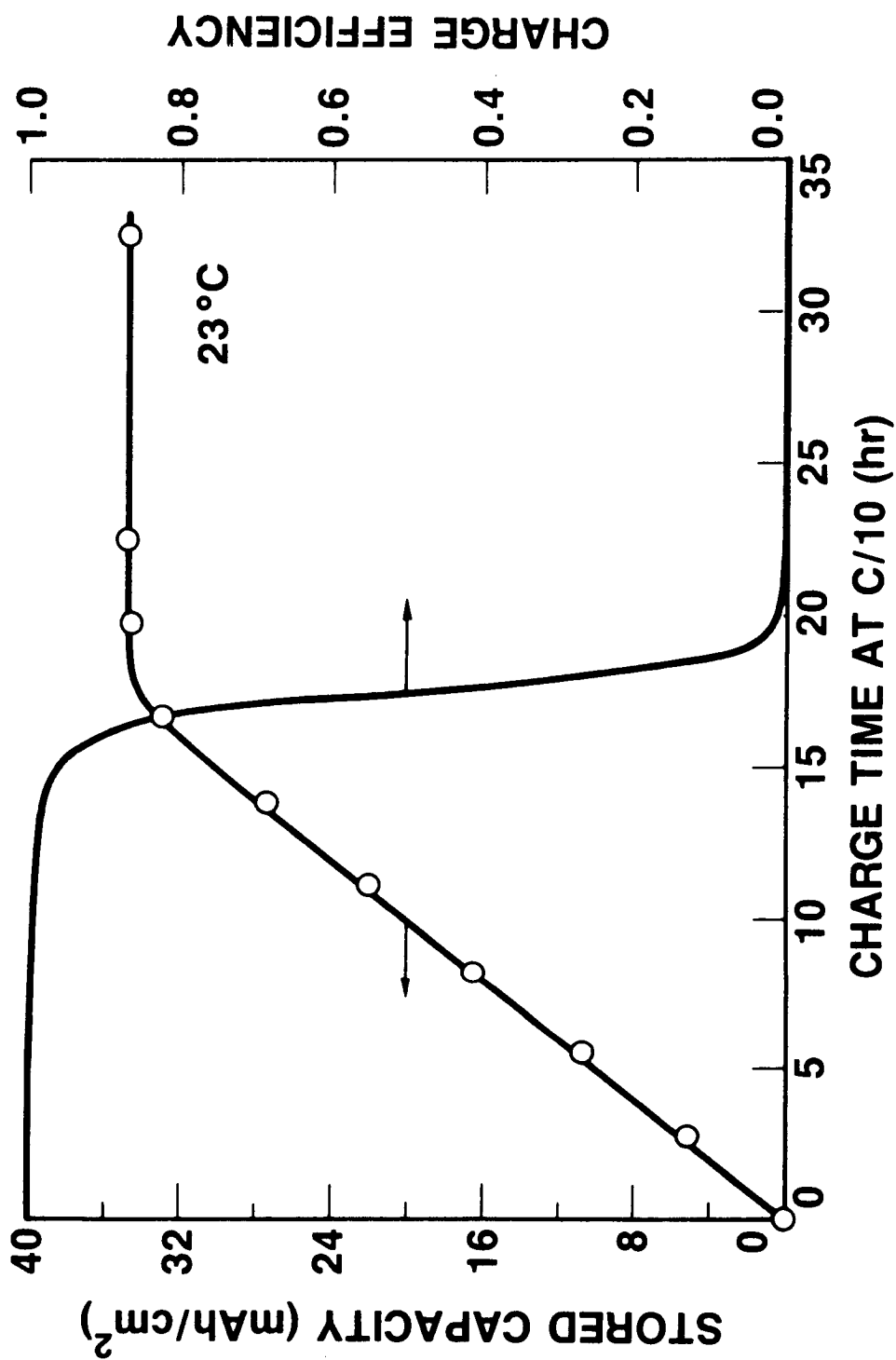


Figure 3.

Capacity and Charge Efficiency as a Function of Charge Time at 0.6A for a 6 Ah NiCd Cell

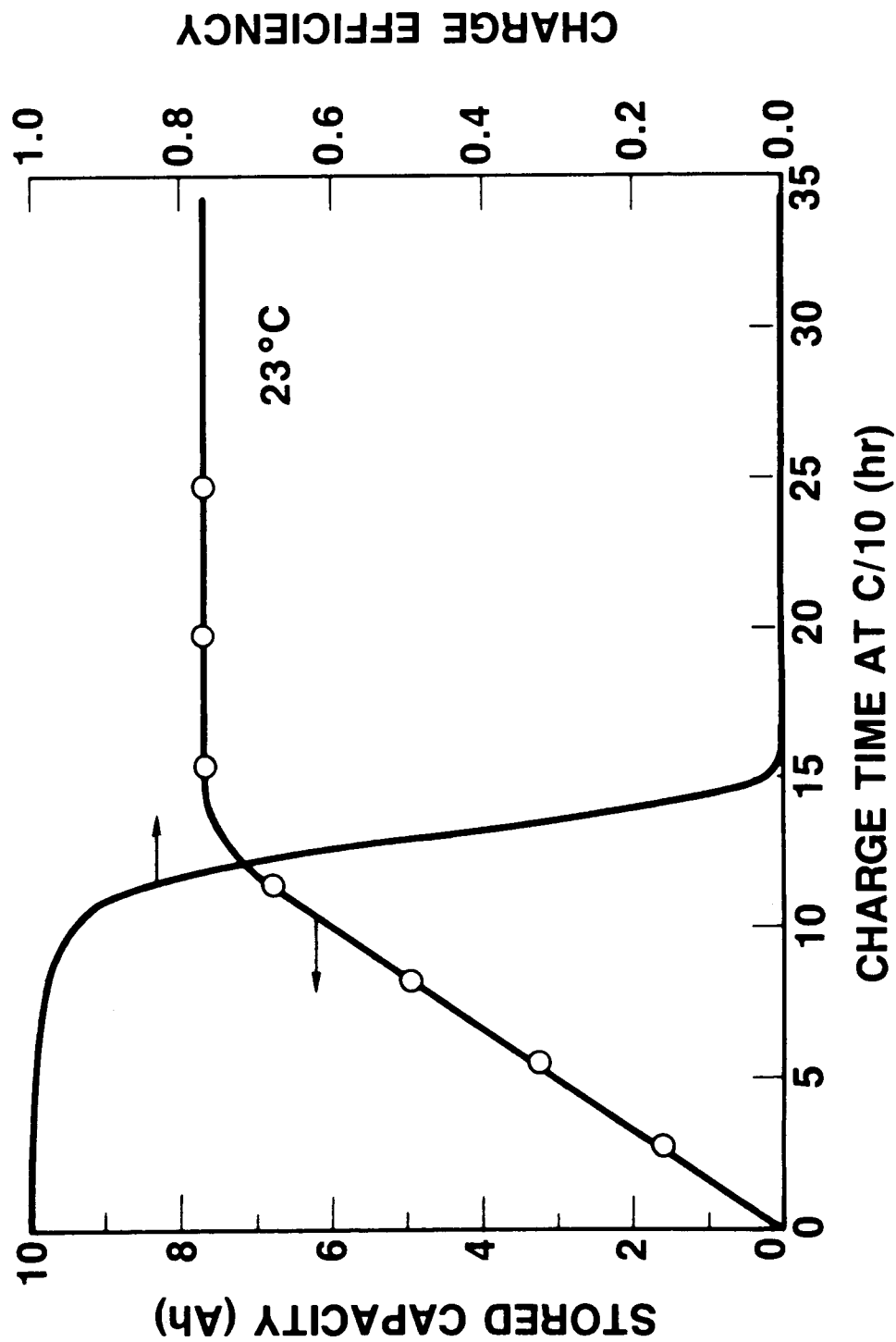


Figure 4.

Predicted Capacity and Charge Efficiency

12 CYCLES FOR NICKEL ELECTRODE AT 0°C CALCULATED FROM VOLTAGE DATA

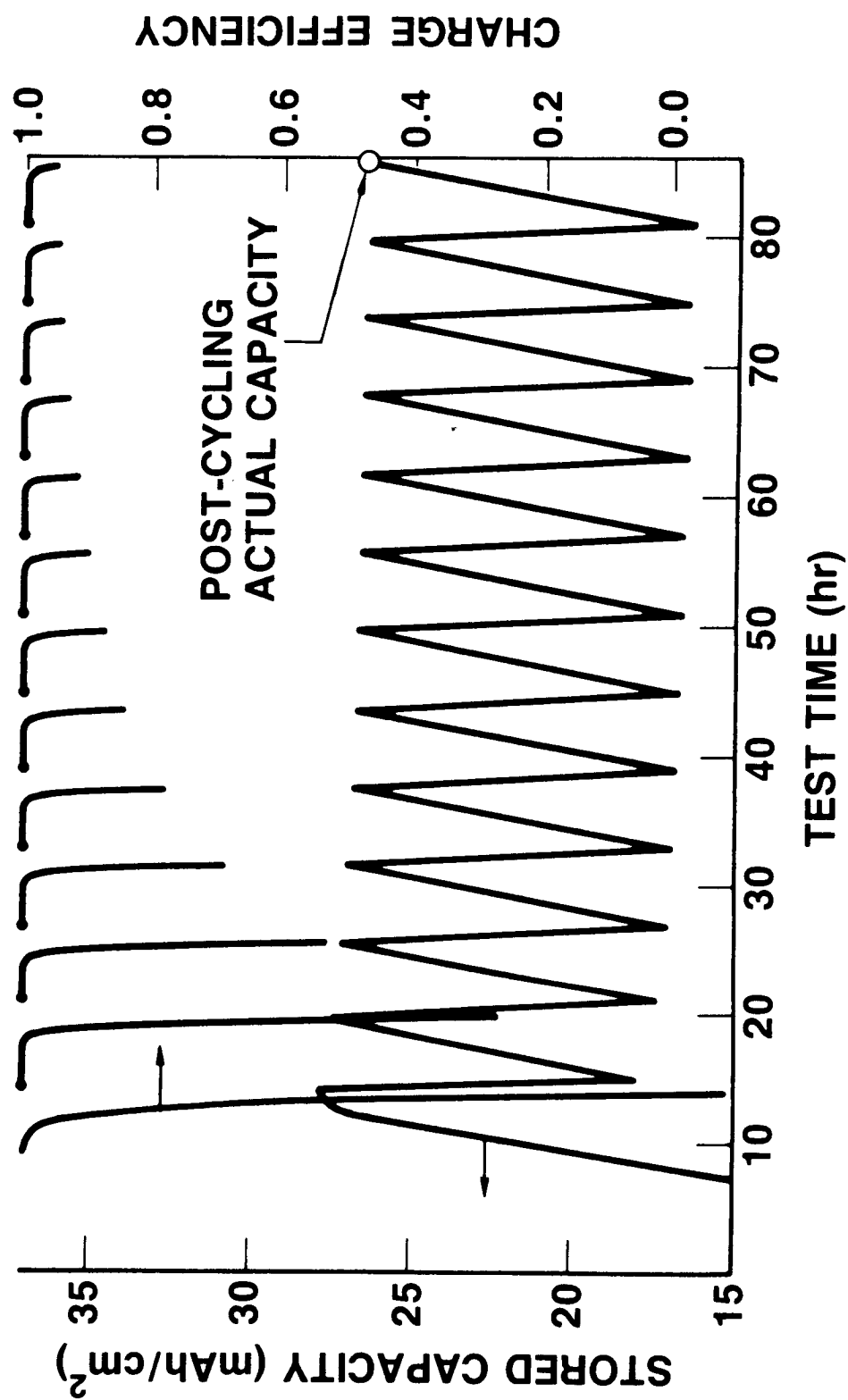


Figure 5.

Predicted Capacity and Charge Efficiency

12 CYCLES FOR 6 Ah NiCd CELL AT 23°C CALCULATED FROM VOLTAGE DATA

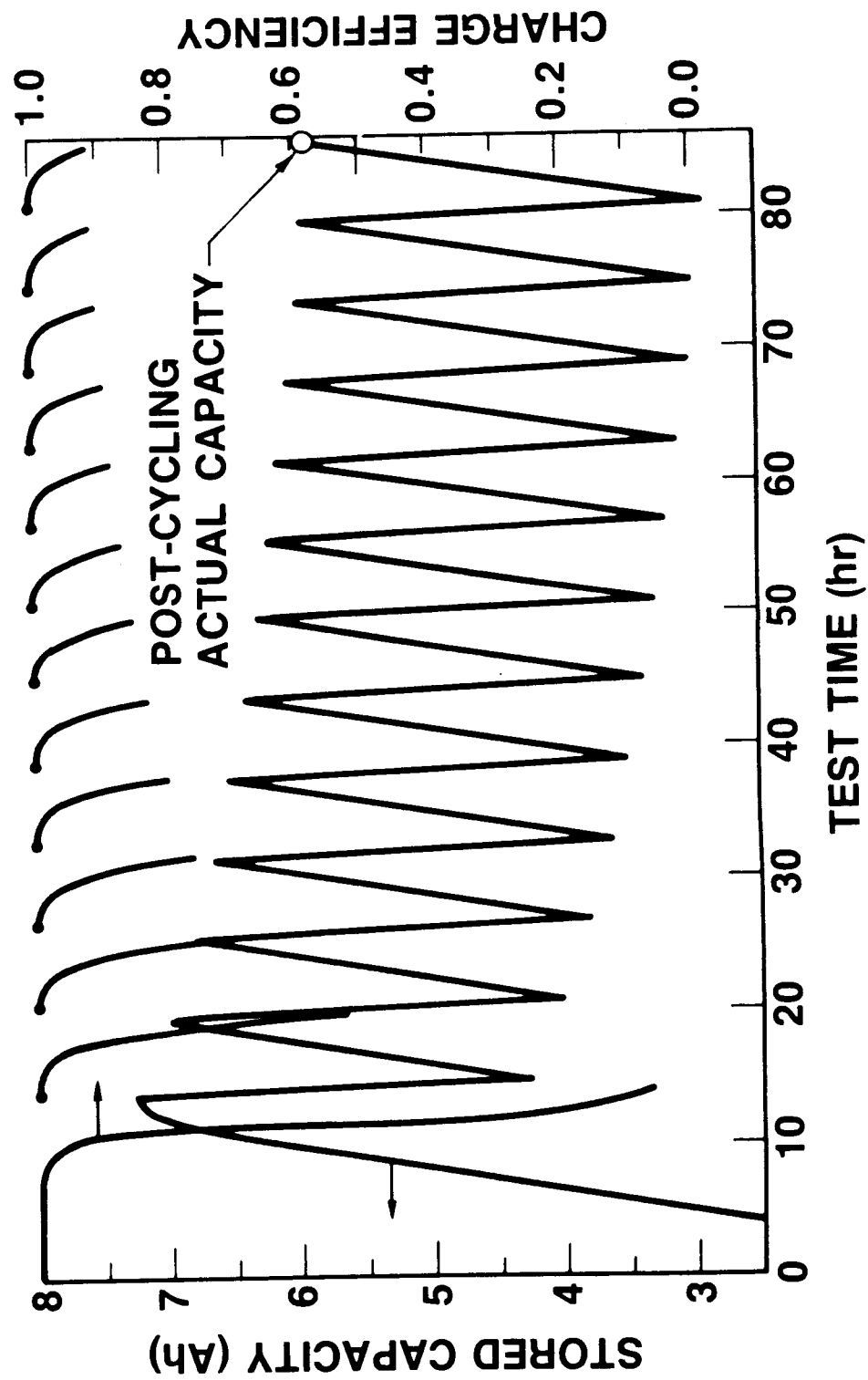


Figure 6.

Real Time Charge Efficiency Monitoring for Nickel Electrodes in NiCd and NiH₂ Cells

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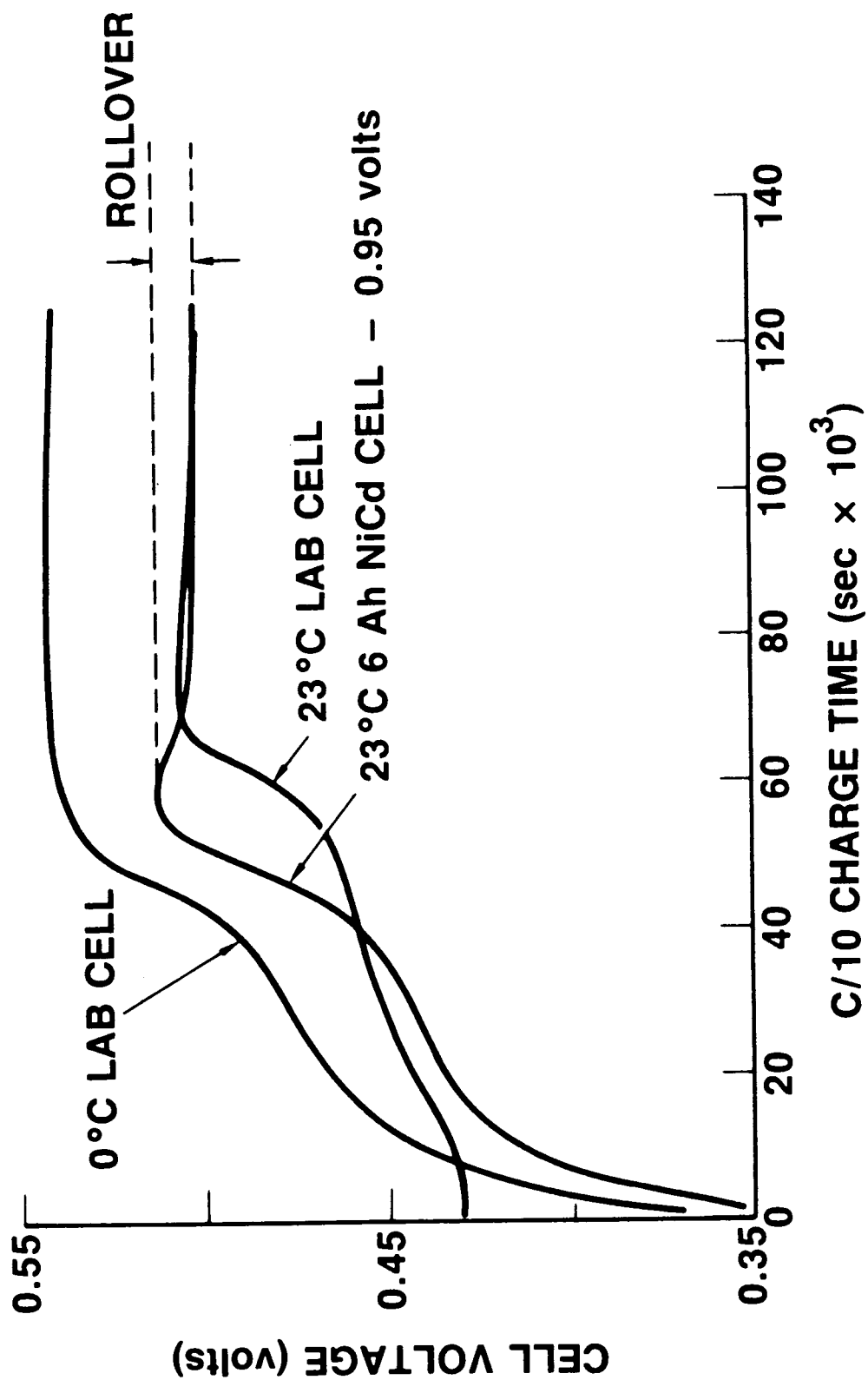
Objectives

- **DEVELOP METHOD FOR ACCURATELY DETERMINING REAL-TIME CHARGE EFFICIENCY**
 - **NICKEL ELECTRODE LIMITED CELLS AT FULLY CHARGED STATE**
- **DEMONSTRATE CAPABILITY TO FOLLOW STATE OF CHARGE DURING CYCLING**
- **METHOD MUST BE EASILY AUTOMATED FOR AUTONOMOUS OR INTELLIGENT POWER SYSTEMS**
 - **DEPENDS ON STANDARD MEASUREMENTS (voltage, current, time) ONLY**

Approach

- CHARGE EFFICIENCY ASSUMED TO BE GOVERNED BY OXYGEN EVOLUTION RATE FROM NICKEL ELECTRODE
 - $\text{EFFICIENCY} = 1 - I_{\text{ox}}/I$
- OXYGEN EVOLUTION RATE CAN BE PREDICTED BASED ON NICKEL ELECTRODE VOLTAGE
 - $I_{\text{ox}} = I_0 e^{\frac{kV}{V_0}}$
- PRIMARY ASSUMPTIONS:
 - CONSTANTS INDEPENDENT OF STATE OF CHARGE
 - NEGATIVE ELECTRODE VOLTAGE NOT AFFECTED BY OXYGEN GENERATED AT POSITIVE

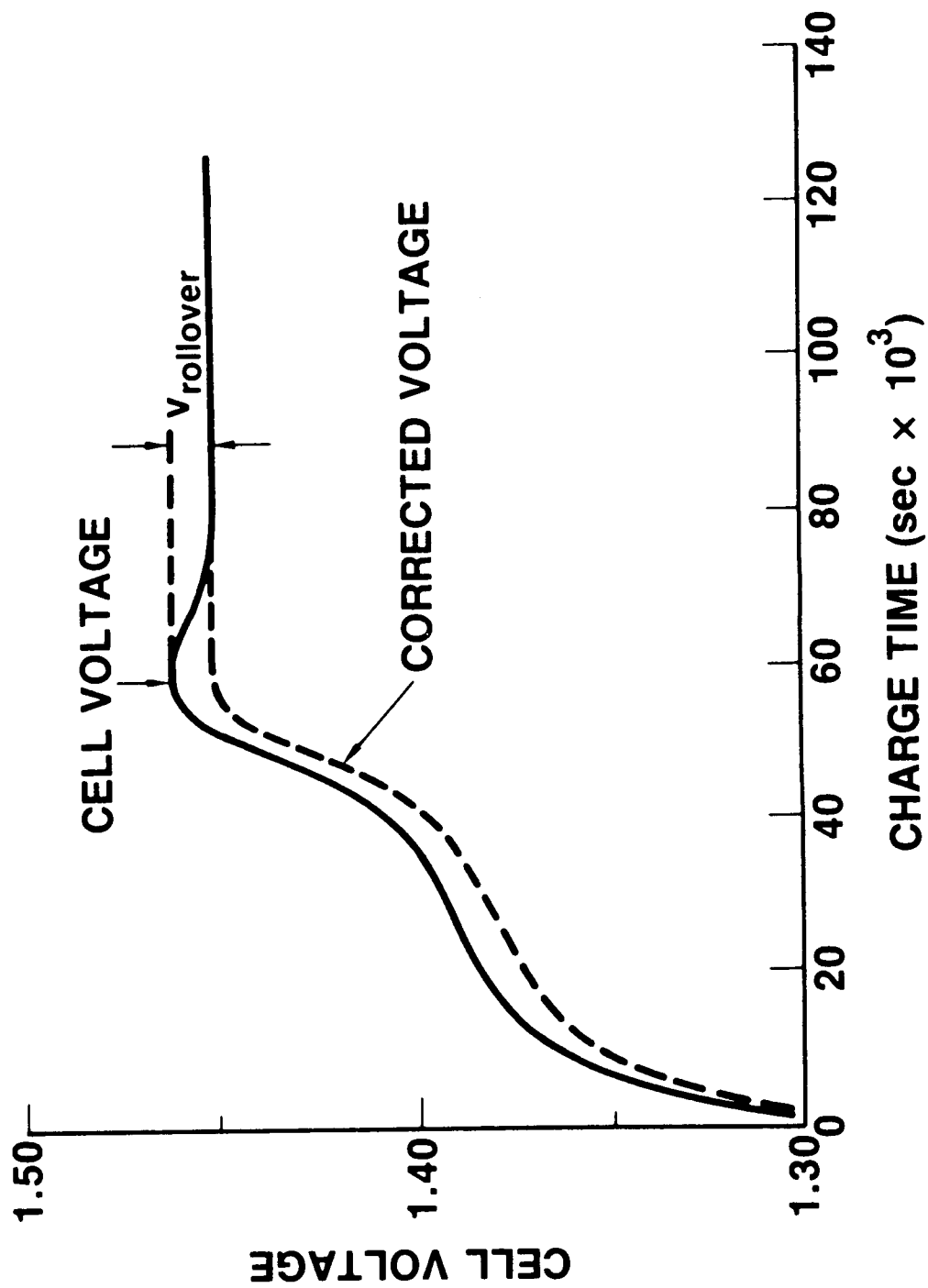
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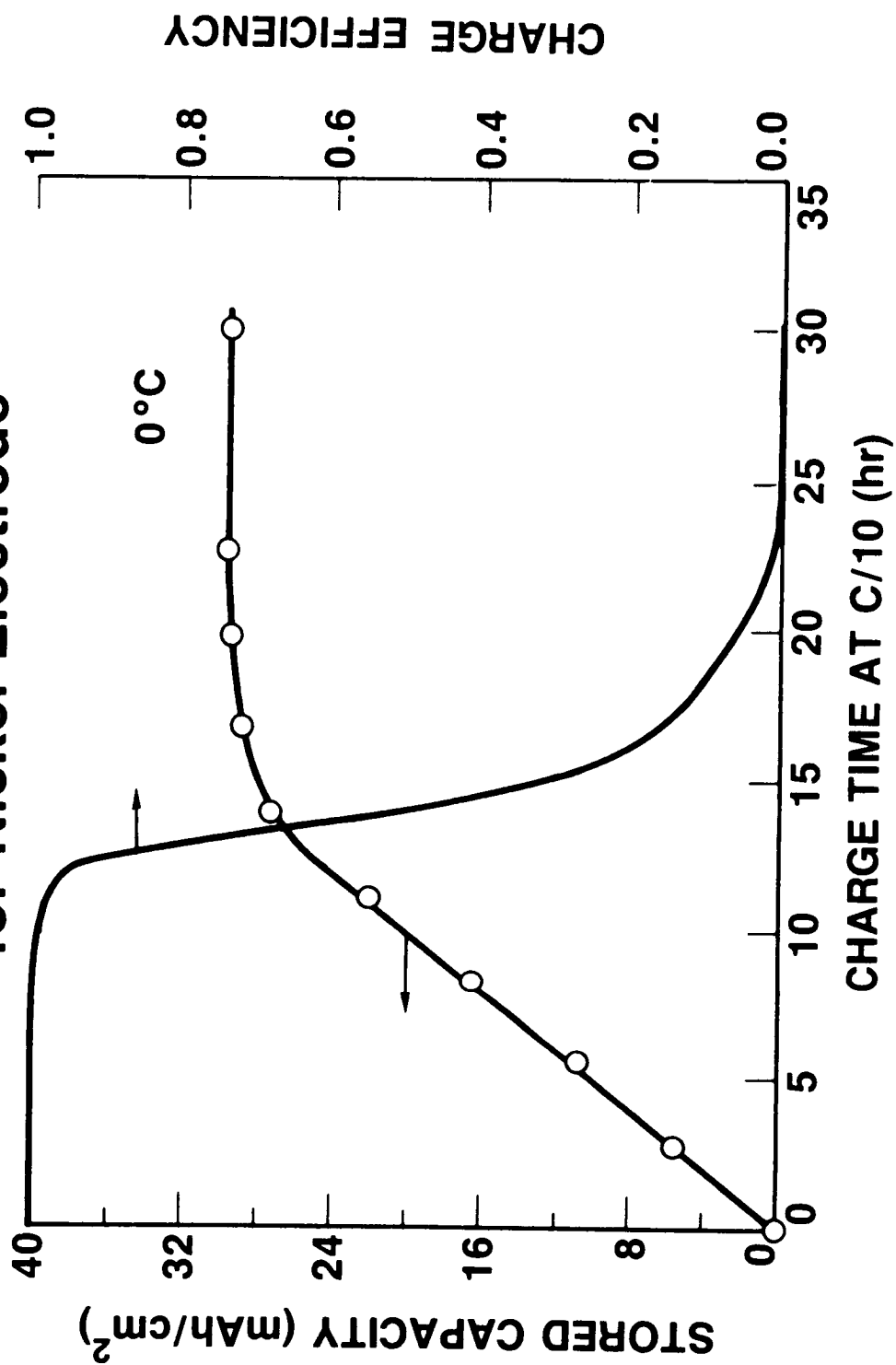
Modified Approach

- ASSUME THAT VOLTAGE ROLLOVER REPRESENTS A NEGATIVE OFFSET TO OXYGEN EVOLUTION VOLTAGE
- CORRECT MEASURED VOLTAGE FOR THIS OFFSET,
 $V' = V - V_{\text{rollover}}$
 - CORRECTION IS NOW A FUNCTION OF STATE OF CHARGE, TEMPERATURE, AND CURRENT

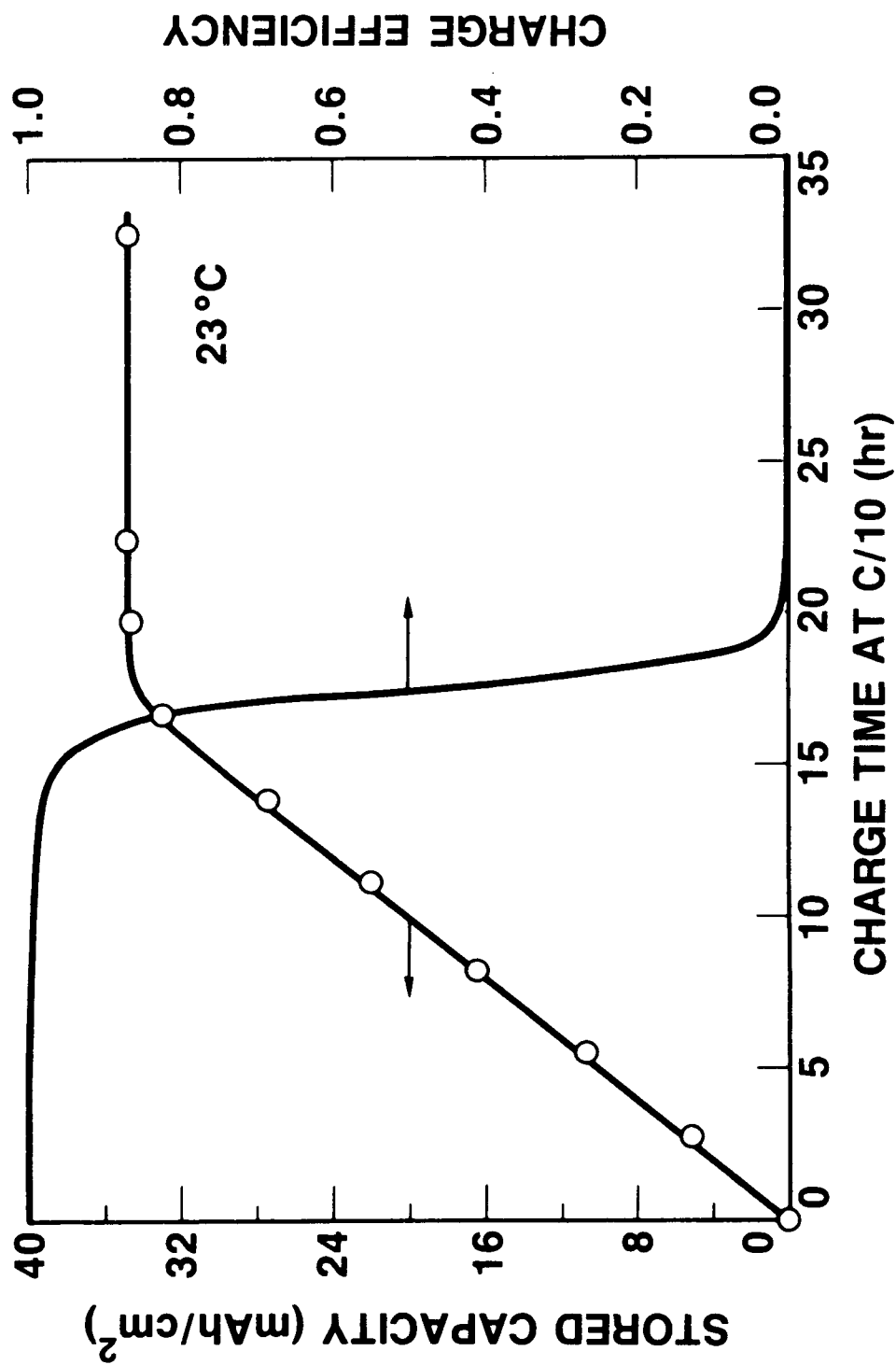
Correction to NiCd Cell Voltage for Rollover, C/10 Charge, 23°C



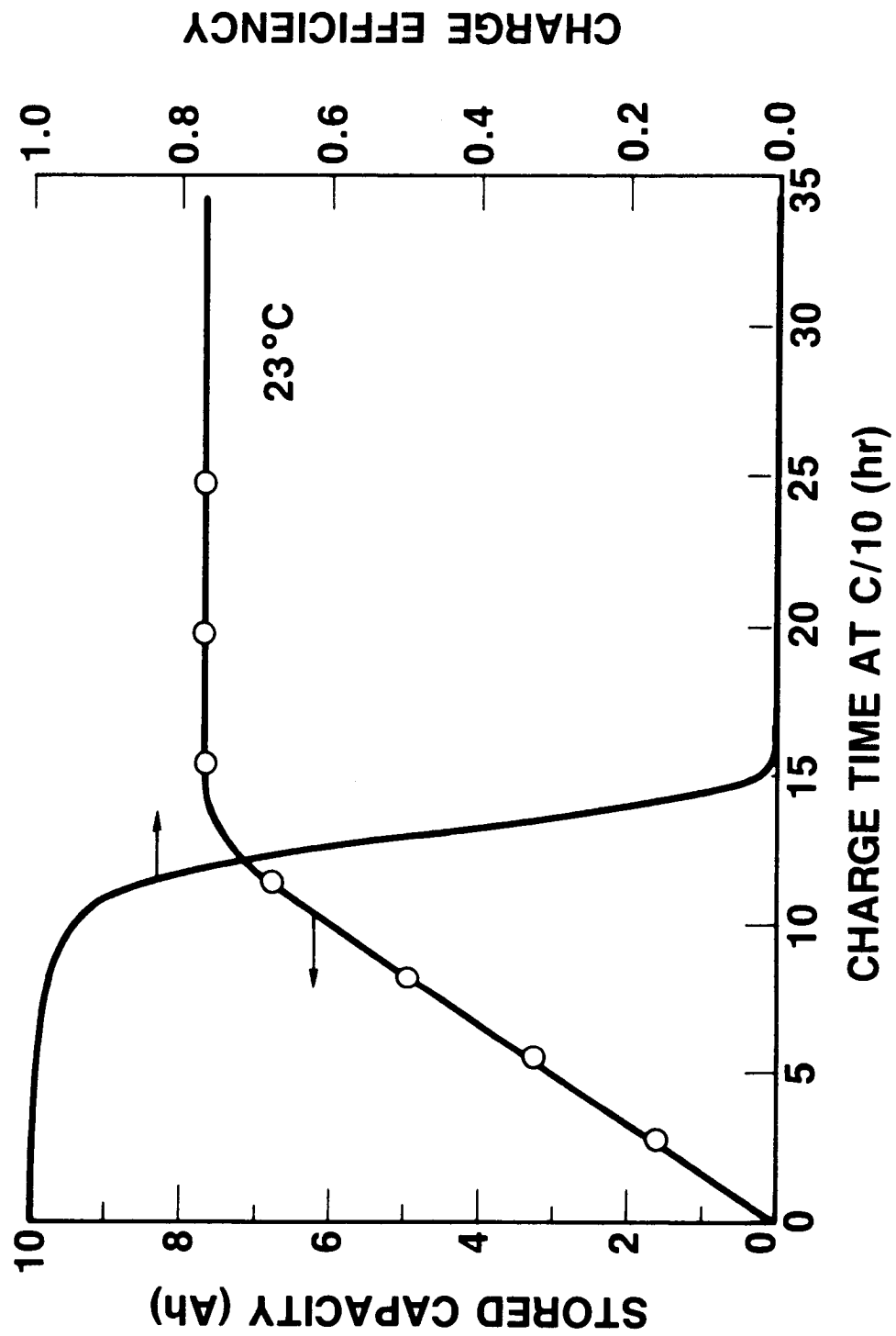
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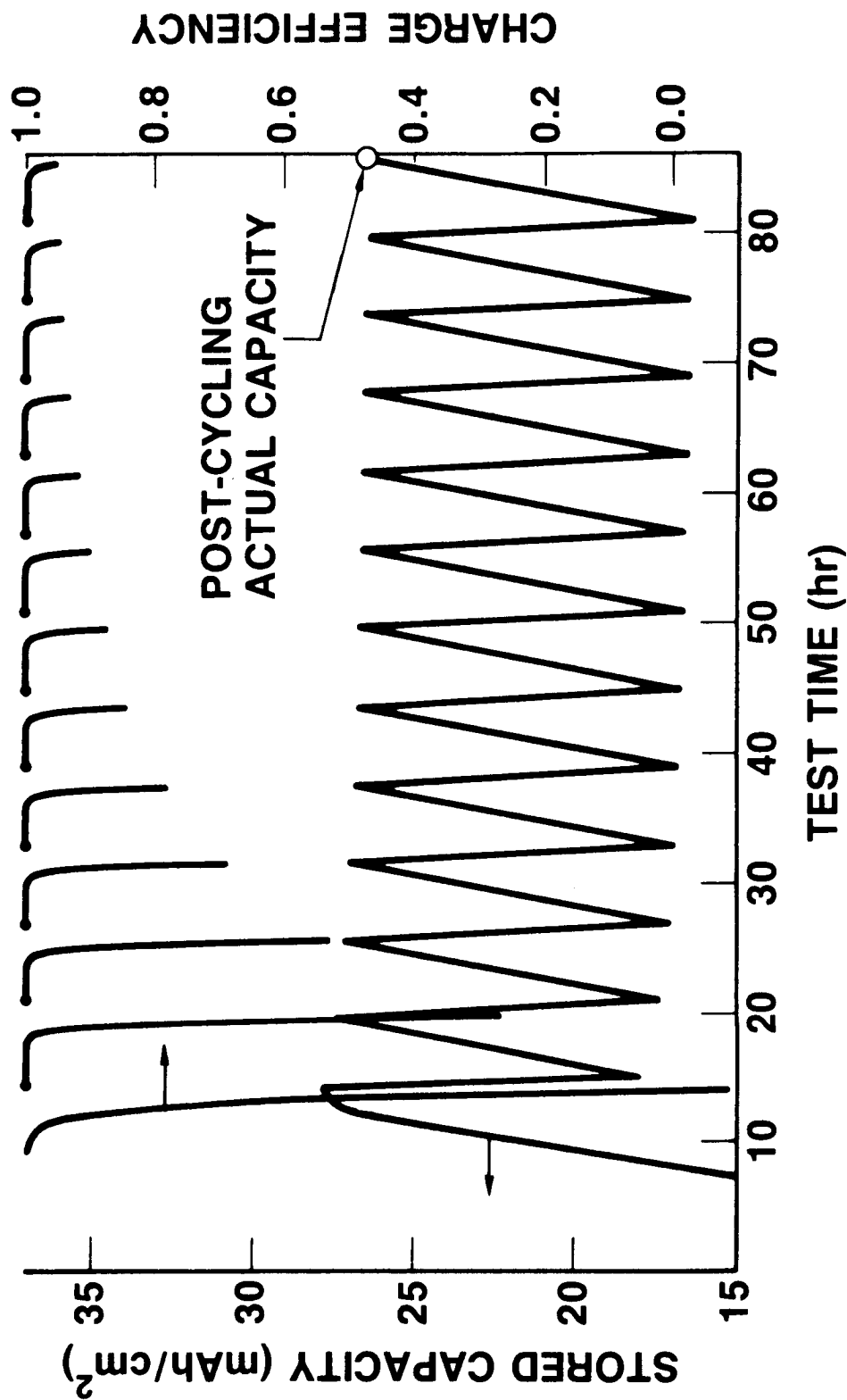


Procedure for Monitoring Charge Efficiency During Cycling Operation

- **CHARGE FULLY AT C/10**
 - DETERMINE ROLLOVER CORRECTION AS FUNCTION OF STATE OF CHARGE
 - DETERMINE OXYGEN EVOLUTION CONSTANTS AFTER FULL CHARGE IS REACHED FROM OVERCHARGE VOLTAGE AT C/10, C/20, C/50, C/100
- **CYCLE 12 TIMES**
 - DISCHARGE 50% OF RATED CAPACITY AT C/2
 - RECHARGE 100% OF CAPACITY DISCHARGED, USING C/10 CHARGE
- **MEASURE STORED CAPACITY AFTER 12 CYCLES**

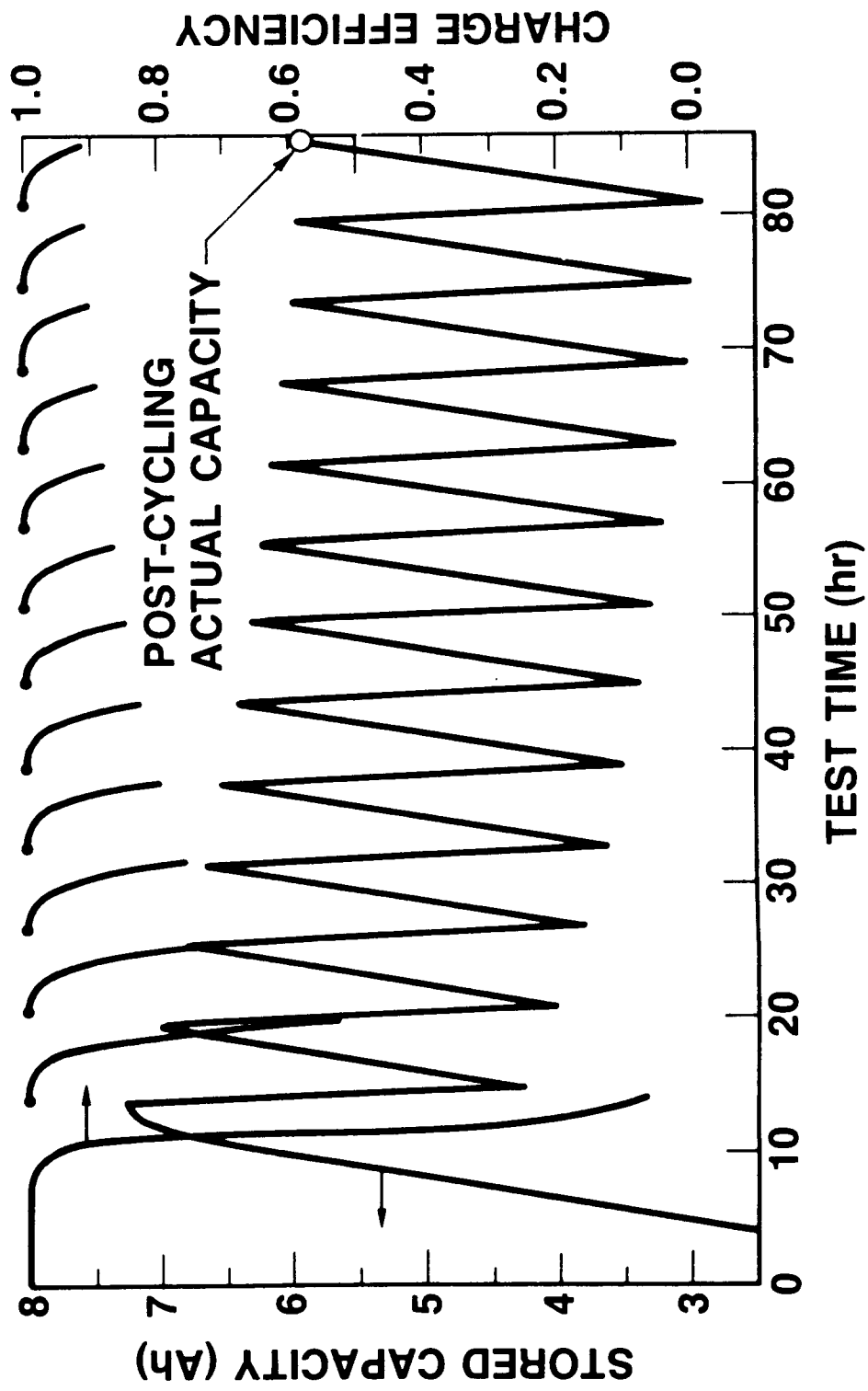
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Predicted Capacity and Charge Efficiency

12 CYCLES FOR 6 Ah NiCd CELL AT 23°C CALCULATED FROM VOLTAGE DATA



Conclusions

- CHARGE EFFICIENCY CAN BE ACCURATELY MONITORED USING NiCd OR NiH₂ CELL VOLTAGES
(Applicable to NiH₂ as well as NiCd)
- METHOD OUTLINED HERE IS SELF-CORRECTING:
 - OXYGEN EVOLUTION POTENTIALS MAY BE PERIODICALLY CHECKED
 - ACCURACY OF METHOD IMPROVES AS CELL STATE OF CHARGE DECREASES
- METHOD SHOULD BE SUITABLE FOR AUTONOMOUS DETECTION OF ANOMALOUS CONDITIONS DURING OPERATION (short circuits, recharge problems, etc.)